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AT CONSTANT PRESSURE—THE REACTION ORDER
AND REACTION RATE

By F. W. STEVENS
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SUMMARY

This investigation was carried out at the Bureau of Standards at the request of and with the financial assistance of the National Advisory Committee for Aeronautics.

1. In the case of the gaseous explosive reaction at constant pressure, the data given in this report show that the statistical expression, $\Gamma = [F]^{n_1} [O_2]^{n_2}$, derived from the order of the stoichiometric equation written for complete combustion of a fuel, is proportional to the spatial rate at which an equilibrium is established in the gaseous explosive system, and that this relation is found to hold for high reaction orders where very complex hydrocarbon fuels are involved in the transformation.

2. The above relation, since it is based solely upon the initial and final condition of the transformation, is independent of the microprocesses, whatever these may be, resulting in the final union of the initial active components in the proportions required by the reaction constant K for the temperature and pressure at which the reaction takes place.

3. The data also provide interesting confirmation of the assumption that high-order reaction processes consist of many simultaneous simpler ones each running its course within the reaction zone "according to its own order and mechanism independently of any other reactions occurring at the same time." The probability of the correctness of this assumption is chiefly shown by the fact that the equivalent reaction order of a composite fuel may be determined from the reaction orders of its components, and further, that the velocity constant, k_F of the fuel may also be determined from the velocity constants of those components.

4. The data given in this report all cover the "explosive limits" of the fuels investigated. Incidental to the purpose of the investigation here reported, the "explosive limits" will be found to be expressed for the condition of constant pressure, in the fundamental terms of concentrations (partial pressures) of fuel and oxygen. It may be seen from the results given that a fundamental relation clearly exists between explosive range and the magnitude of $[F]_{max}$ of the fuel.

The reaction order is given by the stoichiometric equation. This equation expresses quantitatively the equality of masses existing between the initial components and final products of the completed chemical transformation. In the case of a gaseous explosive reaction between a fuel of known composition and oxygen, the equation may thus express the proportions in terms of (atmospheric) partial pressures of the fuel and of the oxygen necessary for complete combustion, but without reference to the ultimate processes by which the transformation is effected. The composition of the final products resulting from the reaction in any particular case is dependent on temperature and pressure and is expressed by the reaction constant K for those conditions:

and

$$K = \frac{[A']^{n'_1} [B']^{n'_2} [C']^{n'_3} \cdot \cdot \cdot \cdot}{[A]^{n_1} [B]^{n_2} [C]^{n_3} \cdot \cdot \cdot \cdot \cdot}$$

$$\left(\frac{\partial ln K_p}{\partial T}\right)_p = \frac{U_p}{RT^2}$$

(Reference 1, p. 223.)

Besides the above thermodynamic relations based on the initial and end conditions of the transformation, the stoichiometric equation has, in connection with the kinetic theory of gases, furnished suggestion for a possible mechanism by which the initial molecular condition of the active components becomes the final condition of the equilibrium products. Following the suggestion made by van't Hoff (Reference 2, p. 13), this kinetic view of the transformation and of its equilibrium condition is indicated in the equation by the use of a modified sign of equality ($\rightleftharpoons$), expressing the direction of the opposed simultaneous reactions that characterize transformations. By this view the total reaction resulting in this thermodynamic equilibrium is the summation of separate simultaneous reactions each having its characteristic order and "each running its course independently of any other reactions occurring at the same time." (Reference 3, p. 877.)

In the case of the simplest reaction orders, and where the reaction may be so conditioned as to run its

course as free as possible from the effects of the container, of variable temperature and concentrations, the correspondence between reaction order and reaction mechanism is usually found to be very close (Reference 4, p. 634, Reference 5, p. 169, Reference 6, p. 2315), and in those cases where a lack of agreement was found, the discrepancy has usually been traced to local changes in concentrations, to impurities, and even to secondary reactions not indicated in the stoichiometric equation which represents only the result of the total chemical change (Reference 7, p. 239).

But in the case of nominally higher reaction orders, where large numbers of molecules may be involved in the transformation, the actual processes taking place are rarely found to follow a mechanism indicated by the reaction order of the stoichiometric equation, although the equilibrium condition agrees with it and the reaction constant is expressed in its terms. The processes taking place in these high-order reactions are found to follow simpler orders. It is found that even trimolecular reactions are rare and that the processes taking place in polymolecular transformations proceed by simultaneous uni, bi, rarely, trimolecular orders. (Reference 4, p. 653.) Moreover, the advance in modern physics has greatly changed the older and cruder concepts of molecular transformations and shown that the microprocesses of a reaction are much more refined than a simple kinetic theory of gases is able to formulate.[1]

The above considerations apply in general to gaseous reactions occurring below ignition temperature where the processes referred to as taking place in a homogeneous gaseous system proceed uniformly throughout the entire mass of active gases. It is assumed that like relationships should apply also to molecular transformations occurring within the zone of explosive reaction, since the initial conditions and final equilibria in both these reaction forms are the same for like conditions of temperature and pressure.

But where the gaseous transformation is brought about by the explosive form of reaction—and this is the form employed in industrial uses of the reaction as a source of power—the gross mechanism of the reaction on which its industrial value depends corresponds more closely with the stoichiometric equation than does the form of reaction below ignition temperature. This is because the rate of transformation of the gaseous system, as brought about by the spatial propagation of the reaction zone within it, is expressed in terms of the spatial rate at which the completed reaction is established in the gases, without reference to the mode or way by which the equilibrium is attained within the reaction zone. Likewise the stoichiometric equation is written for the completed reaction without reference to simultaneous reactions of simple orders that, whatever they may be, lead to the same thermodynamic result; that is, the unknown microprocesses ultimately bring about the union of the active components in the required proportion to produce the resulting equilibrium. This proportion of the active components required for the completed reaction, determines the reaction order, The reaction order then represents a definite final condition and not a process.[2]

If a kinetic interpretation be given the reaction order an expression results that is statistical in form but whose factors are drawn from thermodynamic relations that are independent of the processes involved in the transformation. Nevertheless the empirical kinetic expression obtained from the reaction order possesses this necessary and fundamental requirement: It is consistent with the thermodynamic equilibrium and the reaction constant K is expressed in its terms. If the possible rate Γ indicated by it is seldom consistent with the total rate resulting from unknown microprocesses and simple simultaneous reactions, it does give an expression proportional to their total effect.

In the case of the gaseous explosive reaction at constant pressure the spatial rate s at which an equilibrium is established in the gaseous system is directly determined; so that the proportionality factor k_1 between the probable indicated rate Γ of the reaction order and the actual observed rate s may in any case be foun It is

$$k_1 = \frac{s}{\Gamma}$$

The explosive reaction, $2CO + O_2 = 2CO_2$, offers a concrete example. Its stoichiometric equation expresses a third-order reaction. Its reaction process in one direction (Reference 4, p. 635), as interpreted from the way in which the active components CO and O_2 are found to be united at the completion of the reaction process, is

$$s = k_1 [CO]^2 [O_2]$$

But it is well known that at ordinary initial conditions of temperature and pressure these components will not unite directly to support a zone of explosive reaction. (Reference 3, p. 918.) Their union as expressed in the reaction order must be brought about indirectly by intermediate transformations not indicated in the stoichiometric equation nor by the assumed statistical expression derived from it. The expression $[CO]^2 [O_2]$, designated by Γ, is derived from the completed

[1] "It should be appreciated that even in the case of a complicated set of simultaneous reactions the individual steps of the total process are themselves simple reactions of definite order and mechanism, so that a study of the theory of isolated reactions is the natural preliminary for the study of all branches of chemical kinetics." (Reference 7.)

[2] It has always been found difficult to deduce a reliable dynamic expression from a relation essentially static in its nature, cf. Jouguet, "Vitesse de Reaction et Thermodynamique," Ann. de Physique, v. 5-73 (1926). "The two energy laws may be made use of in the construction of a static system; but they may not be employed in the construction of a dynamic one," Marcelin, "Contribution à l'Etude de la Cinétique Physicochimique," Ann. de Physique III, 120-231 (1915).

condition of the reaction. s is the observed spatial rate at which the reaction is completed in the gaseous system, at constant pressure, by the reaction zone.[3] It represents the continuous summation of the effect of all processes, whatever they may be, simultaneously taking place within the reaction zone. The empirical expression $[CO]^2$ $[O_2]$ is essentially thermodynamic in its origin, as is the stoichiometric equation from which it is derived; the determining time factor in the equation is contained in the value of s which is directly determined. The rate at which the union of 2CO and O_2 is accomplished in consequence of unknown processes occurring within the reaction zone is $s = k_1$ $[CO]^2$ $[O_2]$, where
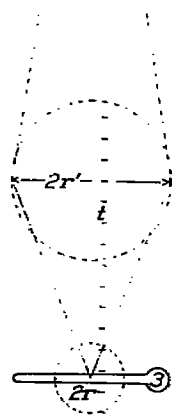
$$k_1 = \frac{s}{\Gamma} = \frac{r^3}{r'^2 t \ [CO]^2 \ [O_2]}$$

The final volume of reaction products represented by r' at initial pressure, but at the temperature due to the explosive reaction, corresponds to the reaction constant K for that pressure and temperature

$$K = \frac{[CO_2]^2}{[CO]^2[O_2]}$$

In obtaining the experimental values of $s = s' \dfrac{r^3}{r'^3}$ for the explosive reaction of these gases at constant pressure it was found that $k_1 = \dfrac{s}{\Gamma}$ not only remained constant for any particular reaction, it was also found in this case to be a fair constant ($=691$) for all values of Γ that would support a zone of explosive reaction. Figure 1, lower curve, shows the close agreement between the observed values of s, represented in the figure by solid dots ●, and the values obtained from

the statistical relation, $s = k_1$ $[CO]^2[O_2]$, represented by open circles ○ and continuous line. ·

The above example shows that the reaction order in this case gives little or no insight as to the processes occurring in the transformation, but it gives reliable information as to their result. The statistical expression based on the reaction order is seen to be proportional to the spatial rate at which the reaction completes itself within the gaseous system. From a practical standpoint such a relationship based on the initial and end points of the transformation is an advantage, for in the use of hydrocarbon fuels as a source of
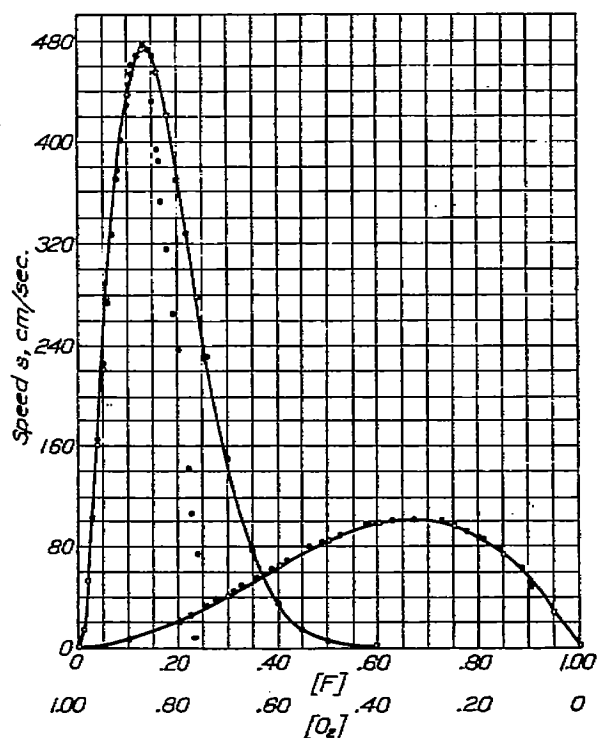

FIGURE 1.—The upper left-hand curve in this figure represents values of s in the butane-oxygen reaction, 2 $C_4H_{10}+13$ $O_2→$. Observed values are indicated by dots. Calculated values, $s=172430$ $[C_4H_{10}]^2$ $[O_2]^{13}$ by open circles and continuous line. In a similar way the lower curve represents values of s in the carbon-monoxide-oxygen explosive reaction, 2 $CO+O_2→$. Observed values are shown by solid circles. Calculated values, $s=691$ $[CO]^2$ $[O_2]$ by open circles and continuous line

power in the gas engine the fuels employed are not only composite but their components for the most part consist of heavy hydrocarbon molecules. The stoichiometric equations for complete combustion of these hydrocarbons represent unusually high reaction orders, involving, as is supposed, complicated sets of simultaneous reactions. The reaction order provides for these cases a statistical expression proportional to the total effect of the unknown microprocesses.

On the assumption that the resulting reaction is the summation of simultaneous reactions each following its own order and mechanism independently of other reactions occurring at the same time within the reaction zone, a stoichiometric equation for complete

[3] A detailed description of the constant pressure bomb and the experimental, arrangement made use of in securing time-volume records of the explosive reaction is given in N. A. C. A. Technical Report No. 176 and in J Am. Chem. Soc. 48, 1806 (1926). The diagrammatic figure here shown and described will be sufficient to indicate the relations of the factors used in the text. If an explosive reaction is initiated by an induction spark within a homogeneous mixture of explosive gases at rest and unconfined the zone of explosive reaction originating at this point propagates itself, for moderate velocities below the velocity of sound, in all directions at constant linear speed, s'. The reaction zone thus forms a spherical shell of flame inclosing the reaction products as formed and expanding at constant linear rate s'. If $2r$ represents a sphere of initial active components ignited at the center, and $2r'$ the resulting sphere of reaction products at the instant the reaction is completed, and t the time interval between the ignition and the completion of the explosive process, then the constant rate of movement of the reaction zone in space will be given by

$$s' = \frac{r'}{t}$$

This is not, however, the rate of propagation of the reaction zone within the gases, since the gases are in motion outward from the center as well as the reaction zone within them. The rate of propagation of the reaction zone relative to the gases as if they were at rest—i. e., the spatial rate of their transformation—is

$$s = s' \frac{r^3}{r'^3} = k_1 [CO]^2 [O_2]$$

combustion of a composite fuel of known components may be written as a simple reaction:

$$n_1F + n_2O_2 = n_3CO_2 + n_4H_2O$$
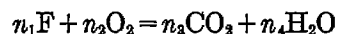
The equivalent order of this reaction, $n_1 + n_2$, is determined from the relative importance of the orders of the separate components of the fuel mixture. The statistical expression derived from this order is

$$\Gamma = [F]^{n_1}[O_2]^{n_2}$$

The rate of propagation of the reaction zone within the explosive mixture of these gases is

$$s = k_1[F]^{n_1}[O_2]^{n_2}$$

The maximum value of s in this expression should be found for the partial pressures of F and O_2 as stated below:

$$s_{max} = k_F \underbrace{\left[\frac{n_1}{n_1+n_2}\right]^{n_1}}_{[F]} \underbrace{\left[1 - \frac{n_1}{n_1+n_2}\right]^{n_2}}_{[O_2]}$$

Experimental data illustrating the relations observed between reaction order and reaction rate in the explosive reaction at constant pressure of composite fuels are given in the tables and coordinate figures that follow.

EXPERIMENTAL RESULTS

The heaviest hydrocarbon fuel found suitable for use at initial atmospheric conditions with a constant pressure bomb was butane, C_4H_{10}. The stoichio-metric equation written for complete combustion of this fuel is

$$2C_4H_{10} + 13O_2 = 8CO_2 + 10H_2O$$
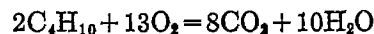
The reaction order is 15. A kinetic interpretation of so high a reaction order would give a probable reaction rate of $\Gamma = [C_4H_{10}]^2[O_2]^{13}$, the probability of so large a number of molecules meeting together being remote. The observed rate of explosive reaction of these gases, however, is high. This would indicate that the total reaction consists of many simpler simultaneous ones, with the result that the fuel and oxygen are found at the completion of the processes to be united, as stated by the equation. How much greater the actual spatial rate s is at which the transformation is effected in the gaseous system than the value of the molecular rate indicated by Γ is

$$k_{C_4H_{10}} = \frac{s}{\Gamma}$$

The observed rate s expressed in terms of the initial partial pressures of the active gaseous components is

$$s = k_{C_4H_{10}}[C_4H_{10}]^2[O_2]^{13}$$

In Table I are recorded the expreimental values of $s = s'\frac{\bar{r}^3}{\bar{r}'^3}$ for those mixtures of butane and oxygen that will ignite. There is also given for each mixture ratio of these gases the corresponding value of Γ and of $k_1 = \frac{s}{\Gamma}$. The value of k_1 found is 172,430 so that $s_{max} = 172,430 [0.133]^2[0.867]^{13} = 477$ cm/sec.

TABLE I.—OBSERVED RATE OF FLAME PROPAGATION IN $2C_4H_{10} + 13O_2 \rightarrow$ EXPLOSIVE REACTION AT CONSTANT PRESSURE

| Record 9-19-28 No. | Partial-pressure atmospheres | | $\Gamma = [C_4H_{10}]^2[O_2]^{13}$ | $s' = \frac{r_1}{t}$ cm/sec | $s = s'\frac{r^3}{r'^3}$ cm/sec | $k_1 = \frac{s}{\Gamma}$ |
	[C$_4$H$_{10}$]	[O$_2$]				
29 to 32	0.040	0.960	0.000942	1,720	164.0	174,200
33 to 40	.050	.950	.001283	2,764	225.5	175,800
41 to 44	.060	.940	.001610	3,587	275.0	174,000
45 to 48	.070	.930	.001910	4,590	327.0	171,500
49 to 56	.080	.920	.002165	5,520	376.5	173,900
57 to 60	.090	.910	.002374	6,214	400.0	168,500
61 to 68	.100	.900	.002539	7,130	431.9	170,100
69 to 72	.109	.891	.002652	7,720	461.0	173,800
73 to 80	.120	.880	.002735	8,132	466.0	170,400
81 to 84	.129	.871	.002762	8,700	478.0	173,100
85 to 92	.140	.860	.002759	8,865	474.0	171,800
Av. k_1						172,430
93 to 96	.150	.850	.002719	8,360	435.0	160,000
97 to 104	.160	.840	.002655	8,049	392.7	148,000
105 to 108	.166	.834	.002605	7,523	352.3	135,200
109 to 116	.180	.820	.002455	6,847	320.8	130,700
117 to 120	.190	.810	.002334	5,988	265.0	113,600
121 to 124	.200	.800	.002198	4,988	236.8	107,800
133 to 140	.220	.780	.001910	2,760	141.0	73,700
141 to 144	.228	.772	.001797	2,148	106.0	59,060
145 to 152	.240	.760	.001625	1,749	72.7	44,730

The results given in the table are shown graphically in the upper left-hand curve of Figure 1. Ordinates in this figure are values of $s = s'\frac{r^3}{r'^3}$; abscissas are partial pressures of fuel and oxygen. Experimental values are represented by dots, $\bullet$. Values of $s = 172,430$ $[C_4H_{10}]^2 [O_2]^{13}$ are shown by open circles and continuous line. The lower curve in this figure represents in a similar way experimental values obtained from records of the explosive reaction $2CO + O_2 \rightarrow$ already mentioned. For this reaction the value of $k_1 = \frac{s}{\Gamma}$ was found to be 691. Values corresponding to the equation $s = 691 [CO]^2 [O_2]$ are represented by open circles and continuous line. The maximum value of s is $691 = [0.667]^2 [0.333] = 103$ cm/sec. Table II gives the experimental values found for this reaction.

TABLE II.—OBSERVED RATE OF FLAME PROPAGATION IN $2CO + O_2 \rightarrow$ EXPLOSIVE REACTION AT CONSTANT PRESSURE

Record 9-7-27 No.	Partial pressure atmospheres		$\Gamma = [CO]^2 [O_2]$	$s' = \frac{r_1}{t}$ cm/sec	$s = s'\frac{r^3}{r'^3}$ cm/sec	$k_1 = \frac{s}{\Gamma}$
	[CO]	[O₂]				
1 to 3	0. 224	0. 776	0. 0389	191	27. 6	709
4 to 7	. 260	. 740	. 0500	226	34. 7	694
8 to 11	. 279	. 721	. 0561	279	37. 5	668
12 to 15	. 310	. 690	. 0663	335	45. 3	683
16 to 19	. 325	. 675	. 0713	365	50. 3	705
20 to 23	. 359	. 641	. 0826	434	55. 5	672
24 to 27	. 388	. 612	. 0921	487	63. 3	687
28 to 31	. 416	. 584	. 1011	561	71. 1	703
32 to 35	. 460	. 540	. 1140	632	80. 3	703
36 to 39	. 491	. 509	. 1227	660	84. 3	687
40 to 43	. 523	. 477	. 1305	715	88. 4	678
44 to 47	. 574	. 426	. 1404	794	99. 8	711
48 to 51	. 622	. 378	. 1463	858	100. 6	688
52 to 55	. 688	. 332	. 1480	870	102. 8	694
56 to 59	. 726	. 274	. 1444	849	101. 9	706
60 to 63	. 775	. 225	. 1351	814	92. 2	682
64 to 67	. 810	. 190	. 1247	733	86. 4	693
68 to 71	. 840	. 160	. 1129	632	79. 2	701
72 to 75	. 848	. 152	. 1093	614	77. 7	711
76 to 79	. 883	. 117	. 0912	463	63. 9	700
80 to 83	. 903	. 097	. 0791	320	50. 1	633
Av. k_1						691

Mixtures of these two gases, carbon monoxide and butane, that differ widely in reaction characteristics, as reaction speed, reaction order, and velocity constant k_1 were made up in various proportions into composite fuels F and examined in the same way as the above simple gases. There is in fact no way to distinguish the time-volume photographic figures of the explosive reaction at constant pressure of different homogeneous explosive mixtures. There is only one reaction zone in any case, and at constant pressure it is propagated at constant speed for moderate velocities below the rate of sound in the gases. To what extent the reaction characteristics of a composite fuel may be predicted from the reaction characteristics of its components on the assumption that the simultaneous reactions occurring within the explosive reaction zone, where each runs its course according to its own order and mechanism "independently of any other reactions occurring at the same time," is shown in the experimental results given below.

A composite fuel F was made up of the two gases in the following proportions: 95 parts by volume of carbon monoxide and 5 parts by volume of butane. The equivalent reaction order of the resulting fuel should then be

0.95 part CO, order 3 = 2.85
.05 part C_4H_{10}, order 15 = .75
Equivalent reaction order = $\overline{3.60}$

The amount of oxygen necessary for complete combustion of one part of the fuel is

0.95 CO $+0.475$ $O_2 = 0.95$ CO_2
.05 $C_4H_{10}+$ .325 $O_2 =$ .20 $CO_2 + 0.25$ H_2O
$\overline{1 F+ .8 \quad O_2 = 1.15 CO_2 + .25 H_2O}$

The stoichiometric equation for this fuel of order 3.6 would be
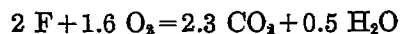
$$2 F + 1.6 O_2 = 2.3 CO_2 + 0.5 H_2O$$

Table III gives the experimental values found for this fuel. $k_F = \frac{s}{\Gamma} = 2,647 \cdot \Gamma = [F]^2 [O_2]^{1.6} \cdot s_{max}$ should then be found for $s = 2,647 [0.555]^2 [0.445]^{1.6} = 223$ cm/sec. Figure 2 shows these results expressed graphically. Observed values of $s = s'\frac{r}{r'}$ are shown in the figure by dots $\bullet$. Calculated values of $s = 2,647$ $[F]^2 [O_2]^{1.6}$ are shown by open circles, O, and continuous line.

TABLE III.—OBSERVED RATES OF FLAME PROPAGATION IN A FUEL F, CONSISTING OF 95 PARTS BY VOLUME OF CARBON MONOXIDE AND 5 PARTS BUTANE, WITH OXYGEN

Record 10-24-28 No.	Partial-pressure atmospheres		$\Gamma=[F]^2[O_2]^{1.8}$	$s'=\frac{r_i}{t}$ cm/sec	$s=s'\frac{r^i}{r^i}$ cm/sec	$k_F=\frac{s}{\Gamma}$
	[F]	[O₂]				
5 to 7	0. 265	0. 735	0. 04291	848	106. 6	2, 531
8 to 11	. 317	. 683	. 05458	1, 252	138. 0	2, 524
12 to 15	. 369	. 631	. 06562	1, 624	178. 0	2, 713
16 to 19	. 412	. 588	. 07258	1, 810	193. 0	2, 660
20 to 23	. 453	. 547	. 07817	2, 194	215. 0	2, 750
24 to 27	. 515	. 485	. 08331	2, 379	223. 0	2, 678
28 to 31	. 571	. 429	. 08415	2, 526	233. 0	2, 771
32 to 35	. 622	. 378	. 08159	2, 401	213. 0	2, 612
36 to 39	. 678	. 322	. 07536	2, 140	195. 0	2. 584
Av. k_F						2, 647
40 to 43	. 733	. 267	. 06495	1, 733	155. 0	2, 390
44 to 47	. 770	. 230	. 05633	1, 054	121. 0	2, 148

In like manner the equivalent order of a fuel consisting of 90 parts by volume of carbon monoxide and 10 parts butane would be

0.90 part CO, order 3, 2.70
.10 part C_4H_{10}, order 15, 1.50
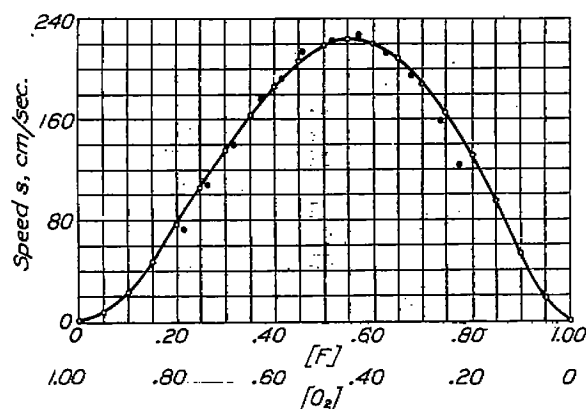
Equivalent order of fuel, 4.20

FIGURE 2.—Represents graphically the results given in Table III. Speeds, s, are plotted as ordinates. Abscissas are partial pressures of the fuel, F and of the oxygen, $O_2(=1-F)$. Observed values of $s=s'\frac{r^i}{r^i}$ are indicated by dots, •. Calculated values of $s=2647\,[F]^2[O_2]^{1.8}$ are shown by open circles and continuous line

The amount of oxygen necessary for complete combustion of one part of this fuel is

0.90 CO + 0.45 O_2 = 0.90 CO_2
.10C_4H_{10}+ .65 O_2 = .40 CO_2+0.5 H_2O
1F   +1.1 O_2 =1.3 CO_2+ .5 H_2O
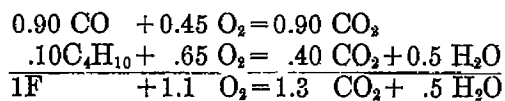
Its stoichiometric equation written for order 4.2 would be
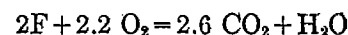
$$2F+2.2\,O_2=2.6\,CO_2+H_2O$$

Table IV gives the experimental values obtained with this fuel. The value found for $k_F=\frac{s}{\Gamma}$ is 4,652.
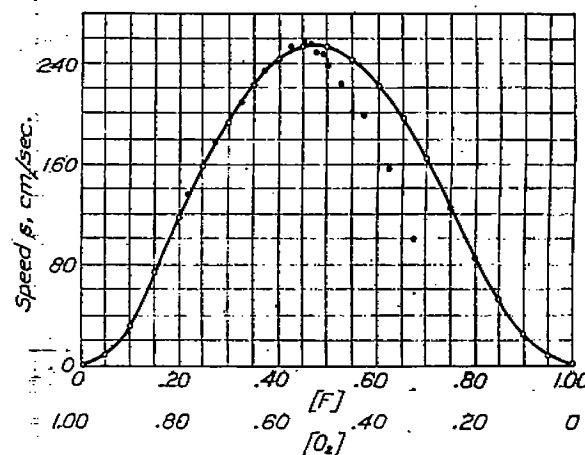

FIGURE 3.—The results given in Table IV are plotted in Figure 3. Observed values, $s=s'\frac{r^i}{r^i}$ are shown by dots •. Calculated values, $s=4652\,[F]^2[O_2]^{1.8}$ are indicated by the continuous line

$\Gamma=[F]^2[O_2]^{2.2}$. In Figure 3 the curve represented by a continuous line corresponds to the equation $s=4,652\,[F]^2[O_2]^{2.2}$. Observed values of s are shown by the mark •. $s_{max}=4,652\,[0.476]^2\,[0.524]^{2.2}=254$ cm/sec.

TABLE IV.—OBSERVED VALUES OF THE RATE OF FLAME PROPAGATION IN A FUEL F, MADE UP OF 90 PARTS BY VOLUME OF CARBON MONOXIDE AND 10 PARTS BUTANE WITH OXYGEN

Record 10-27-28 No.	Partial-pressure atmospheres		$\Gamma=[F]^2 [O_2]^{3.1}$	$s'-\frac{r_1}{t}$ cm/sec	$s-s'\frac{r^2}{r^1}$ cm/sec	$k_1=\frac{s}{\Gamma}$
	[F]	[O₂]				
1 to 4	0.220	0.780	0.02802	1,260	136	4,804
5 to 8	.273	.727	.03960	1,875	177	4,470
9 to 12	.321	.679	.04397	2,270	210	4,741
13 to 16	.370	.630	.04954	2,748	233	4,712
17 to 20	.427	.573	.05356	3,311	254	4,747
21 to 24	.455	.545	.05445	3,303	255	4,685
25 to 28	.465	.535	.05464	3,428	256	4,680
29 to 32	.475	.525	.05468	3,116	248	4,529
33 to 36	.485	.515	.05463	3,116	246	4,500
Av. k_1						4,652
37 to 40	.495	.505	.05451	3,088	237	4,353
41 to 45	.525	.475	.05336	2,998	223	4,188
46 to 49	.575	.425	.05034	2,515	198	3,936
50 to 53	.621	.379	.04561	2,012	157	3,440
54 to 57	.674	.326	.03858	1,173	100	2,592

A fuel whose composition is 80 parts by volume carbon monoxide and 20 parts butane has an equivalent reaction order of 5.4. Its stoichiometric equation written for this order and for complete combustion would be

$$2F+3.4 O_2=3.2 CO_2+2 H_2O$$
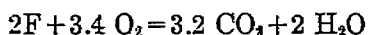
The experimental results obtained from the explosive reaction of this fuel are given in Table V. The value

for $\Gamma=[F]^2 [O_2]^{3.4}$. The value for $k_F=\frac{s}{\Gamma}=12,136$. The value for s_{max} would then be

$$s_{max}=12,136 [0.370]^2 [0.630]^{3.4}=345 \text{ cm/sec.}$$

These results are also shown graphically in Figure 4. Observed values of s are marked •. Calculated values of $s=12,136 [F]^2 [O_2]^{3.4}$ are given by the curve marked by a continuous line.

TABLE V.—OBSERVED VALUES OF THE RATE OF FLAME PROPAGATION IN A FUEL F, MADE UP OF 80 PARTS BY VOLUME OF CARBON MONOXIDE AND 20 PARTS BUTANE, WITH OXYGEN

Record 10-30-28 No.	Partial-pressure atmospheres		$\Gamma=[F]^2 [O_2]^{3.4}$	$s'-\frac{r_1}{t}$ cm/sec	$s-s'\frac{r^4}{r^2}$ cm/sec	$k_1=\frac{s}{\Gamma}$
	[F]	[O₂]				
1 to 4	0.136	0.864	0.01125	1,274	143	12,690
5 to 8	.175	.825	.01593	1,983	190	11,940
9 to 12	.110	.890	.00814	757	98	12,070
12 to 16	.159	.841	.01403	1,586	171	12,200
17 to 20	.218	.782	.02060	2,967	255	12,400
21 to 24	.277	.723	.02606	4,009	300	11,780
25 to 28	.324	.676	.02771	4,731	345	12,440
29 to 32	.353	.647	.02836	5,098	338	11,910
33 to 36	.365	.635	.02845	5,072	345	12,120
37 to 40	.375	.625	.02845	5,079	334	11,780
41 to 44	.384	.616	.02839	5,184	340	12,170
Av. k_1						12,136
45 to 48	.396	.604	.02824	5,063	317	11,700
49 to 52	.426	.574	.02748	4,668	300	10,910
53 to 56	.475	.525	.02524	3,733	233	9,239
57 to 60	.526	.474	.02186	2,381	152	6,942

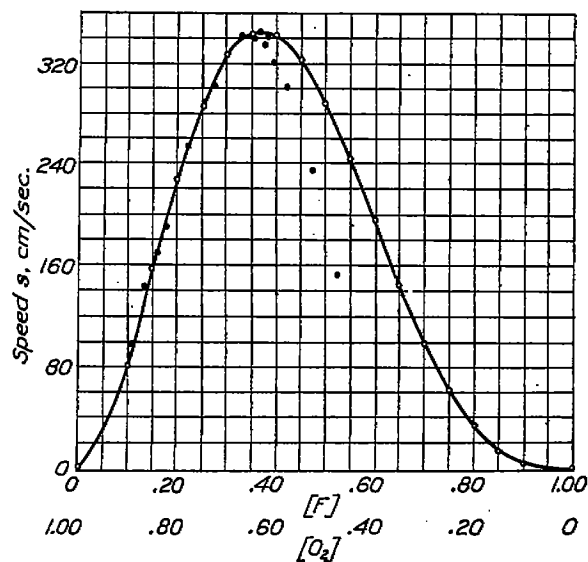A composite fuel made up of 70 parts by volume of carbon monoxide and 30 parts butane has an equiva-

FIGURE 4.—Shows the results given in Table V. The open circles and continuous line is the curve corresponding to the equation $s=12136[F]^2[O_2]^{3.4}$. The solid circles, •, near this line are observed values of $s=s'\frac{r^4}{r'^4}$

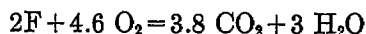lent reaction order of 6.6. Its stoichiometric equation for this order and for complete combustion will be

$$2F + 4.6\ O_2 = 3.8\ CO_2 + 3\ H_2O$$

Table VI gives the experimental results obtained from the explosive reaction of this fuel. The value for Γ

is $[F]^2 [O_2]^{4.6}$. The value for $k_F = \frac{s}{\Gamma} = 21,848$. The value for s_{max} is

$$s_{max} = 21,848\ [0.300]^2\ [0.700^{4.6} = 381\ cm/sec.$$

These results are shown graphically in Figure 5. Observed values are marked •. The locus of the
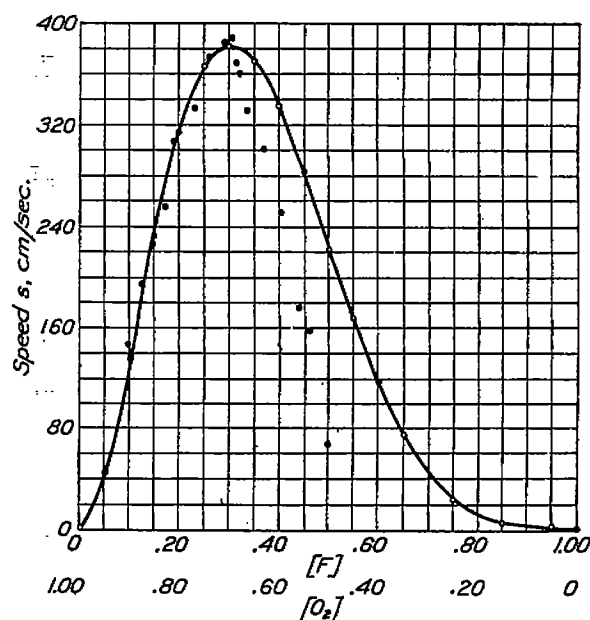

FIGURE 5.—Represents the values given in Table VI expressed as a graph. Observed values are shown as solid circles. Calculated values corresponding to the equation, $s=21848\ [F]^2\ [O_2]^{4.6}$ are shown by the continuous line and open circles

equation 21,848 $[F]^2\ [O_2]^{4.6}$ is shown by the continuous curve.

TABLE VI.—OBSERVED VALUES OF THE RATE OF FLAME PROPAGATION IN A FUEL F, MADE UP OF 70 PARTS BY VOLUME OF CARBON MONOXIDE AND 30 PARTS BUTANE, WITH OXYGEN

Record 11-5-28 No.	Partial-pressure atmospheres		$\Gamma=[F]^2[O_2]^{4.6}$	$s'=\frac{r_1}{t}$ cm/sec	$s=s'\frac{r^4}{r'^4}$ cm/sec	$k_F=\frac{s}{\Gamma}$
	[F]	[O_2]				
1 to 4	0.098	0.902	0.005975	1,181	139	23,230
5 to 8	.144	.876	.008362	2,010	193	23,090
9 to 12	.129	.851	.010566	2,474	225	21,300
13 to 16	.175	.825	.012650	2,992	254	20,090
17 to 24	.194	.806	.013920	4,177	308	22,120
25 to 28	.238	.762	.016230	5,321	332	20,450
29 to 32	.266	.734	.017060	5,340	372	21,800
33 to 36	.290	.710	.017410	5,932	386	22,170
37 to 40	.307	.693	.017430	6,303	390	22,380
Av. k_1						21,848
41 to 44	.315	.685	.017410	6,054	365	20,970
45 to 47	.325	.675	.017320	6,037	359	20,720
48 to 52	.338	.662	.017140	5,875	330	19,260
53 to 56	.375	.625	.016180	5,153	309	19,100
57 to 60	.404	.596	.015090	4,320	250	16,560
61 to 64	.439	.561	.013530	3,148	174	13,720
65 to 68	.468	.532	.012010	2,177	158	13,160
69 to 72	.496	.504	.010520	1,117	66	6,284

Table VII gives results observed in the reaction of a fuel made up of 60 parts by volume of carbon monoxide and 40 parts butane, The equivalent reaction order of this fuel with oxygen for complete combustion is 7.8. Its stoichiometric equation written for this order is

$$2F + 5.8\ O_2 = 4.4\ CO_2 + 4\ H_2O$$
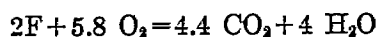
In this case, $\Gamma = [F]^2\ [O_2]^{5.8} \cdot k_F = \frac{s}{\Gamma} = 36,870$. The value for s_{max} should then be

$$s_{max} = 36,870\ [0.256]^2\ [0.744]^{5.8} = 435\ \text{cm/sec}$$

Figure 6 expresses these results in graphic form. Observed values determined from the photographic figures, $s = s' \frac{r^3}{r'^3}$ are marked •. Values calculated from the statistical relation $s = 3,687\ [F]^2 \cdot [O_2]$ are marked by the continuous curve.
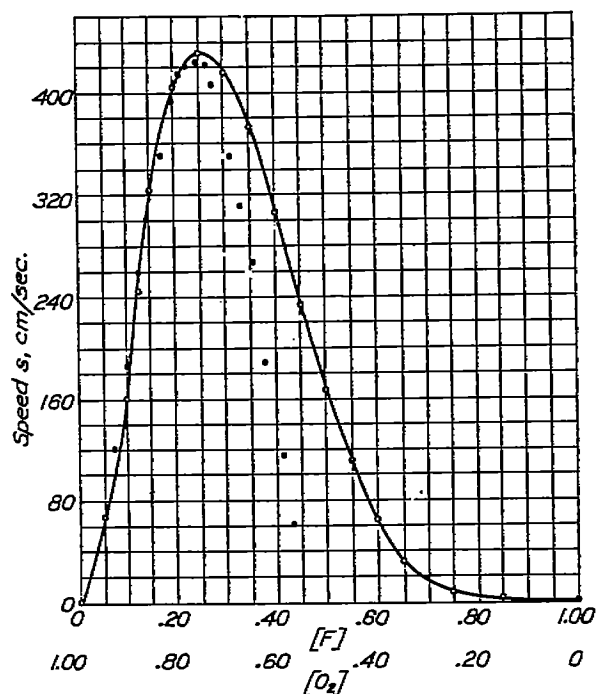

FIGURE 6.—Expresses the results given in Table VII in graphic form. The continuous curve is the locus of all values of s in the relation $s=36870\ [F]^2\ [O_2]^{5.8}$. Experimental values obtained from the photographic figures are represented by dots, •

TABLE VII.—OBSERVED VALUES OF THE RATE OF FLAME PROPAGATION IN A FUEL F, MADE UP OF 60 PARTS BY VOLUME OF CARBON MONOXIDE AND 40 PARTS BUTANE, WITH OXYGEN

Record, 11-8-28 No.	Partial pressure atmospheres		$\Gamma=[F]^2\ [O_2]^{5.8}$	$s'=\frac{r_1}{t}$ cm/sec	$s=s'\frac{r^3}{r'^3}$ cm/sec	$k_1=\frac{s}{\Gamma}$
	[F]	[O₂]				
1 to 4	0.069	0.931	0.003142	1,046	122	38,810
5 to 8	.095	.905	.005055	1,772	187	36,970
9 to 12	.119	.881	.006792	2,846	262	38,530
13 to 16	.145	.855	.008480	3,954	303	35,750
17 to 20	.171	.829	.009861	5,066	351	36,420
21 to 24	.195	.805	.010798	5,282	391	36,220
25 to 28	.210	.790	.011230	3,932	416	37,030
29 to 32	.225	.775	.011540	6,220	420	36,380
33 to 36	.236	.764	.011690			
37 to 40	.245	.755	.011750	6,422	423	35,980
41 to 44	.255	.745	.011800	6,663	432	36,620
Av. k_1						36,870
45 to 48	.263	.737	.011790	6,560	420	35,620
49 to 52	.275	.725	.011700	6,607	408	34,860
53 to 56	.304	.696	.011280	6,065	350	31,030
57 to 60	.329	.671	.010696	5,223	311	29,030
61 to 64	.355	.645	.009910	4,418	267	26,580
65 to 68	.378	.622	.008690	3,351	188	21,650
69 to 72	.408	.592	.007916	2,087	115	14,580
73 to 76	.423	.577	.007372	949	60	8,180

When the composite fuel consists of equal parts by volume of the components carbon monoxide and butane, its equivalent reaction order is 9. A stoichiometric equation written for this order and for complete combustion is

$$2 \text{ F} + 7 \text{ O}_2 = 5 \text{ CO}_2 + 5 \text{ H}_2\text{O}$$
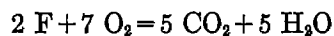
The values for Γ will then be written $\Gamma = [\text{F}]^2 [\text{O}_2]^7$, and the value for $k_F = \frac{S}{\Gamma} = 52,757$. s_{max} will be

$$s_{max} = 52,757 \; [0.222]^2 \; [0.778]^7 = 450$$

Figure 7 is a graphic statement of these results and their relation drawn from the experimental values given in Table VIII.

TABLE VIII.—OBSERVED RATE OF PROPAGATION OF REACTION ZONE IN A FUEL F, CONSISTING OF 50 PARTS BY VOLUME OF CARBON MONOXIDE AND 50 PARTS BUTANE WITH OXYGEN

| Record 11-12-28 No. | Partial-pressure atmospheres | | $\Gamma = [\text{F}]^2 [\text{O}_2]^7$ | $s' = \frac{r_1}{t}$ cm/sec | $s = s'\frac{r^4}{r'^4}$ cm/sec | $k_F = \frac{s}{\Gamma}$ |
	[F]	[O]				
1 to 4	0. 049	0. 951	0. 00169	900	86. 9	51, 430
5 to 8	. 075	. 925	. 00326	1, 756	167. 3	51, 370
9 to 12	. 096	. 904	. 00455	2, 640	246. 0	54, 140
13 to 16	. 125	. 875	. 00614	4, 720	325. 0	52, 920
17 to 20	. 150	. 850	. 00721	5, 553	374. 0	52, 270
21 to 24	. 166	. 834	. 00774	6, 442	411. 0	53, 150
25 to 28	. 165	. 835	. 00771	6, 408	419. 0	54, 320
29 to 32	. 196	. 804	. 00835	7, 570	434. 0	52, 030
33 to 36	. 209	. 791	. 00847	7, 496	450. 0	53, 180
Av. k_F						52, 757
41 to 44	. 230	. 770	. 00849	7, 491	418. 0	49, 180
45 to 48	. 257	. 743	. 00803	6, 773	371. 0	46, 110
49 to 52	. 289	. 711	. 00768	5, 475	273. 0	35, 600
53 to 56	. 314	. 686	. 00691	4, 989	238. 0	34, 440
57 to 60	. 346	. 654	. 00613	2, 985	149. 0	24, 280
61 to 64	. 380	. 620	. 00509	1, 474	117. 0	23, 030
65 to 68	. 420	. 580	. 00389	451	45. 0	11, 570

When the composition of the fuel is 30 parts carbon monoxide by volume and 70 parts butane, the equivalent reaction order is 11.4. The stoichiometric equation written for the fuel of this order and for complete combustion is

$$2 \text{ F} + 9.4 \text{ O}_2 = 6.2 \text{ CO}_2 + 7 \text{ H}_2\text{O}$$

$\Gamma = [\text{F}]^2 [\text{O}_2]^{11.4} \cdot k_F = \frac{s}{\Gamma} = 92,978$ and s_{max} will be found for the relation

$$s_{max} = 92,978 \; [0.175]^2 \; [0.824]^{9.4} = 467$$

Table IX gives the experimental results obtained from the reaction of this fuel. Figure 8 is their graphic representation where observed values of $s = s' \frac{r^3}{r'^3}$ are marked by dots • and calculated values $s = 92,978 \; [\text{F}]^2 \; [\text{O}_2]^{9.4}$ are marked by a continuous line.
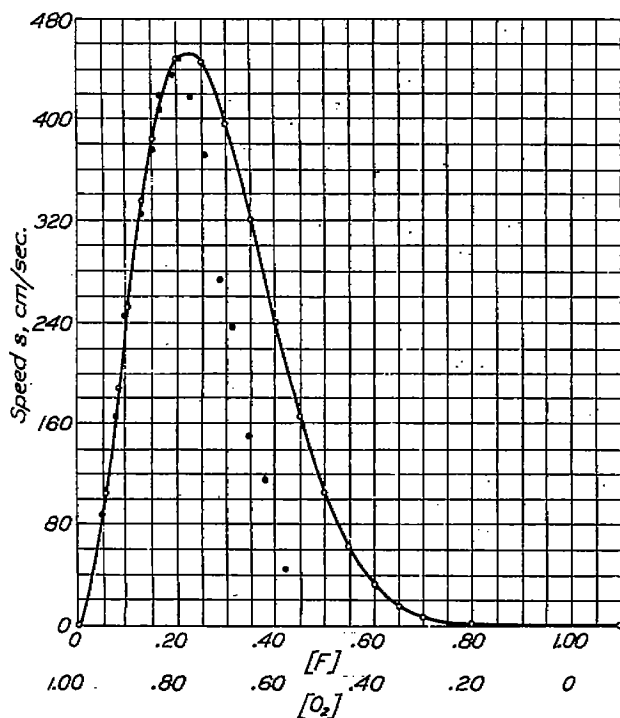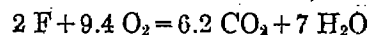
FIGURE 7.—Is a graphical statement of the values and relationships given in Table VIII. The locus of all s-values in the relation $s = 52757 \; [\text{F}]^2 \; [\text{O}_2]^7$ are shown by the continuous curve. Observed values of s are represented by dots, •

TABLE IX.—OBSERVED RATES OF FLAME PROPAGATION IN A FUEL F, CONSISTING OF 30 PARTS BY VOLUME OF CARBON MONOXIDE AND 70 PARTS BUTANE, WITH OXYGEN

Record 11-15-28 No.	Partial-pressure atmospheres		$\Gamma=[F]^2 [O_2]^{11.8}$	$s'=\dfrac{r_1}{t}$ cm/sec	$s=s'\dfrac{r_1^2}{r_2^2}$ cm/sec	$k_F=\dfrac{s}{\Gamma}$
	[F]	[O₂]				
1 to 4	0. 0427	0. 9573	0. 001211	1, 010	109	90, 020
5 to 8	. 0452	. 9548	. 001322	1, 356	129	97, 610
9 to 12	. 0608	. 9392	. 002052	2, 041	204	99, 490
13 to 16	. 0852	. 9148	. 003141	3, 905	305	97, 750
17 to 20	. 1110	. 8890	. 004077	5, 582	379	93, 110
21 to 24	. 1320	. 8680	. 004604	6, 653	414	89, 850
25 to 28	. 1570	. 8430	. 004924	8, 035	445	90, 680
29 to 32	. 1700	. 8300	. 005015	7, 995	428	85, 310
Av. k_F						92, 978
33 to 36	. 1800	. 8200	. 005015	7, 362	403	80, 280
37 to 40	. 2050	. 7950	. 004868	6, 958	365	75, 060
41 to 44	. 2290	. 7710	. 004553	6, 442	313	68, 690
45 to 48	. 2560	. 7440	. 004068	4, 619	258	63, 410
49 to 52	. 2800	. 7200	. 003650	3, 508		
53 to 56	. 3060	. 6940	. 003024	1, 867	102	33, 770

For a composite fuel made up of 10 parts by volume of carbon monoxide and 90 parts butane the equivalent

FIGURE 8.—The values given in Table IX are plotted in Figure 8. Observed values of $s=s'r'^3$ are shown by dots, •. The locus of all s-values in the relation $s=92978$ [F]² [O₂]⁹·⁴ are shown by the continuous curve

reaction order is 13.8. Its stoichiometric equation written for this order and for complete combustion is

$$2 \text{ F}+11.8 \text{ O}_2=7.4 \text{ CO}_2+9 \text{ H}_2\text{O}$$

Table X gives the observed results obtained from the reaction of this fuel.　$\Gamma=[F]^2 [O_2]^{11.8}$.　$k_F=\dfrac{s}{\Gamma}=143,020$,
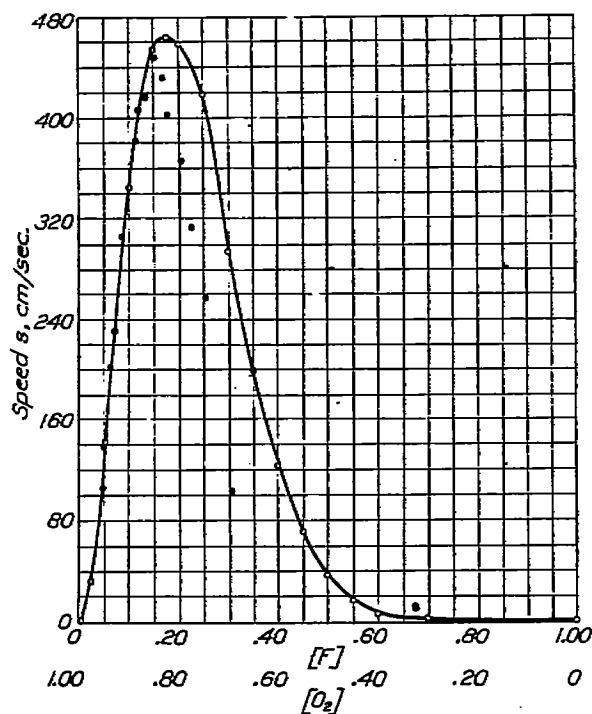
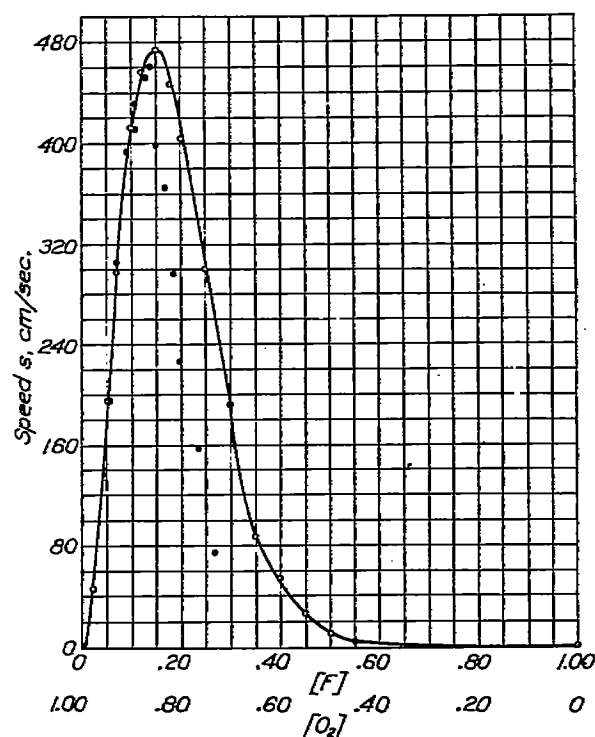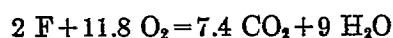$$s_{max}=143,020 \ [0.145]^2 \ [0.855]^{11.8}=473$$

FIGURE 9.—Gives the values recorded in Table X in the form of a graph. The observed values of s are represented by dots, •. The curve represented by the continuous line corresponds to the equation $s=143020$ [F]² [O₂] ¹¹·⁸

Figure 9 represents these results graphically. Observed values are marked •. Values obtained from the equation 143,020 [F]² [O₂]¹¹·⁸ are represented by the continuous line on the figure.

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TABLE X.—OBSERVED RATES OF FLAME PROPAGATION IN A FUEL F, CONSISTING OF 10 PARTS BY VOLUME OF CARBON MONOXIDE AND 90 PARTS BUTANE, WITH OXYGEN

| Record 11-27-28 No. | Partial-pressure atmospheres | | $\Gamma=[F]^2[O_2]^{11.4}$ | $s'=\frac{r_1}{t}$ cm/sec | $s=s'\frac{r_1^2}{r^2}$ cm/sec | $k_F=\frac{s}{\Gamma}$ |
	[F]	[O²]				
5 to 8	0. 050	0. 950	0. 001364	2, 412	195	142, 600
9 to 12	. 070	. 930	. 002082	4, 259	307	146, 200
13 to 16	. 090	. 910	. 002650	5, 670	373	140, 600
17 to 20	. 111	. 889	. 003073	6, 590	432	140, 600
21 to 24	. 130	. 870	. 003264	8, 280	452	138, 300
29 to 32	. 140	. 860	. 003306	8, 820	460	139, 000
Av. k_F						143, 020
33 to 36	. 150	. 850	. 003304	7, 881	398	120, 600
37 to 40	. 170	. 830	. 003208	7, 476	364	113, 600
41 to 44	. 186	. 814	. 003049	6, 494	297	97, 520
45 to 48	. 209	. 791	. 002748	5, 050	226	82, 150
49 to 52	. 239	. 761	. 002276	3, 235	156	68, 480
53 to 56	. 264	. 736	. 001873	1, 476	75	41, 130

A relation was also sought connecting the k_F value of the fuel with the k_1 values of the fuel's components. Such a relation is found to be a simple one for the case
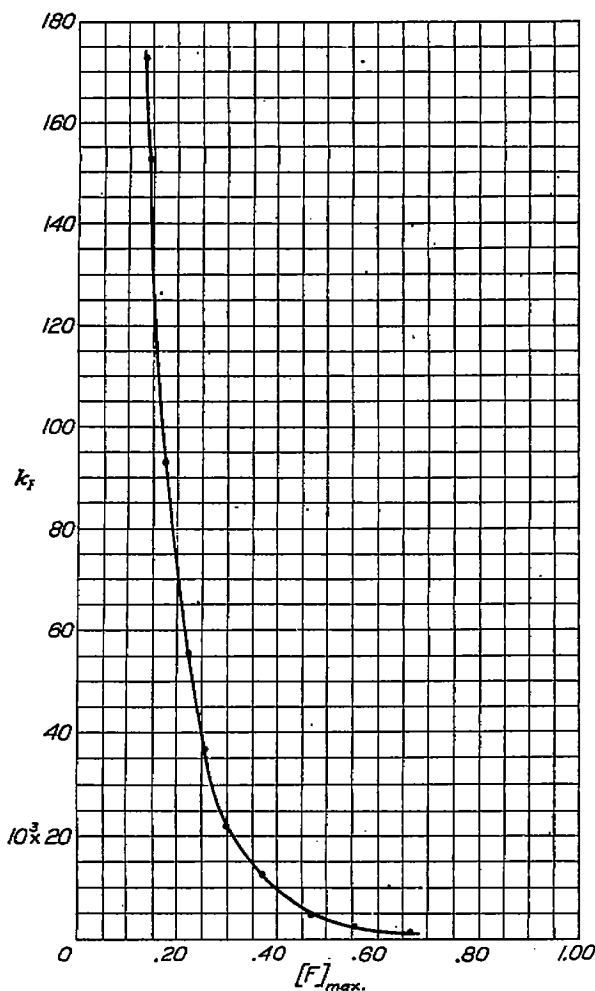

FIGURE 10.—The curve in this figure, determined from the experimental values found for k_F, shows graphically the effect of the reaction orders of the fuels components on the velocity constant, k_F of fuels made up of carbon monoxide and butane

where the reaction orders of the fuel's components are all the same. The reaction order of any fuel consisting of these components will then be the same as that of the components. (Reference 8, p. 15) so that

$$s = k_F [F]^{n_1} [O_2]^{n_2}$$

All of the factors to the right in the above equation may be known from the velocity coefficients of the reaction zone of the components and the mixture ratio of F and O_2. That is, the rate of propagation of the reaction zone in any mixture ratio of F and O_2 may be predicted for any composite fuel made up of components having the same reaction order.
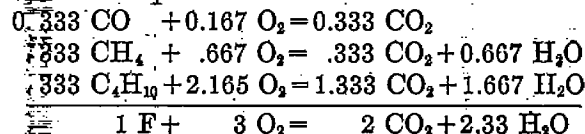
When, however, the reaction orders of the components of the fuel differ greatly, the equivalent reaction orders of the various possible mixtures made of these components will vary between the least and greatest reaction order to be found among its components. This may be seen from the records given above, and made more evident by the curve in Figure 10.

In order to show that the relations given above hold for composite fuels made up of many known components, there is given below one example of a set of result obtained from a fuel made up of three components—carbon monoxide, methane, and butane. In the example given, the fuel consisted of equal parts by volume of these components. The equivalent reaction order of this fuel is
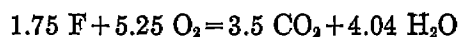
0. 333 part CO, order   = 1
 . 333 part CH_4 order   3 = 1
 . 333 part C_4H_{10} order   15 = 5
                                        ——
Equivalent order of fuel F = 7

The proportion of O_2 necessary for complete combustion of one part fuel is

0.333 CO   + 0.167 O_2 = 0.333 CO_2
.333 CH_4 + .667 O_2 = .333 CO_2 + 0.667 H_2O
.333 C_4H_{10} + 2.165 O_2 = 1.333 CO_2 + 1.667 H_2O
——————————————————————————
1 F + 3 O_2 = 2 CO_2 + 2.33 H_2O

Its stoichiometric equation written for order 7 is

1.75 F + 5.25 O_2 = 3.5 CO_2 + 4.04 H_2O

Observed results for this reaction are given in Table XI. $\Gamma=[F]^{1.75}[O_2]^{5.25}\cdot k_F=\frac{s}{\Gamma}=23,532$. The value for s_{max} is

$$s_{max}=23,532 [0.25]^{1.75} [0.75]^{5.25}=460 \text{ cm/sec}$$

These results, plotted in the same manner as those already given, are shown in Figure 11.

TABLE XI.—OBSERVED VALUES OF THE RATE OF FLAME PROPAGATION IN A FUEL F, MADE UP OF 33.3 PARTS BY VOLUME OF CARBON MONOXIDE, 33.3 PARTS METHANE, AND 33.3 PARTS BUTANE WITH OXYGEN

| Record 4-20-29 No. | Partial-pressure atmospheres | | $\Gamma=[F]^{1.71}[O_2]^{5.28}$ | $s'=\dfrac{r_1}{t}$ cm/sec | $s=s'\dfrac{r_1}{r'_1}$ cm/sec | $k_F=\dfrac{s}{\Gamma}$ |
	[F]	[O₂]				
5 to 8	0.080	0.920	0.00777	1,545	164	21,680
9 to 12	.110	.890	.01140	2,792	275	24,160
13 to 16	.140	.860	.01451	3,746	340	23,430
16' to 19	.160	.840	.01621	4,930	388	23,910
20 to 23	.181	.819	.01761	5,669	414	23,500
23' to 26	.204	.796	.01869	6,814	448	23,970
27 to 30	.223	.777	.01911	7,268	458	23,820
31 to 34	.238	.762	.01948	7,381	466	23,930
35 to 38	.250	.750	.01952	7,460	455	23,330
39 to 42	.257	.743	.01950	7,528	460	23,590
Av. k_F						23,532
43 to 46	.280	.720	.01921	6,955	391	20,360
47 to 50	.310	.690	.01835	5,797	342	18,650
51 to 54	.335	.665	.01610	5,017	279	16,100
55 to 58	.368	.632	.01564	3,570	212	13,530
59 to 62	.403	.597	.01360	1,464	93	6,850
63 to 67	.427	.573	.01213	839	53	4,383

REMARKS

Deviations from statistical equation, $s=k_F$ $[F]^{n_1}$ $[O_2]^{n_2}$.—It will be noticed in all of the tables as well as in all of the coordinate figures given—except those for the $2CO+O_2\rightarrow$ reaction—that the observed values of $s=s'\dfrac{r^3}{r'^3}$ fall short of the calculated values of $s=k_F$ $[F]^{n_1}$ $[O_2]^{n_2}$ after passing the mixture ratio for s_{max}, and that this deviation from a theoretical value increases with increasing amounts of the hydrocarbon in excess of the theoretical amount of oxygen for complete combustion. The stoichiometric equation is written for complete combustion of the fuel. Complete combustion does not take place when the fuel is in excess of the required amount of oxygen. Besides, the excess of a hydrocarbon or of carbon in the highly heated products of combustion containing water vapor is not an inert substance, as is an excess of CO in the equilibrium products, CO_2 of the $2CO+O_2\rightarrow$ explosive reaction, nor the excess of O_2, always present, in the reaction products below the reaction for s_{max}. A reaction takes place between the excess of the hydrocarbon and water vapor that is not accounted for in the stoichiometric equation written for complete combustion, nor in the statistical expression that determines the theoretical curve. Similar deviations from a theoretical reaction constant K, due to the presence in the reacting system of an inert gas or to the dissociation of the products of reaction, led finally, when the causes of these deviations were better understood and suitable devices provided for their investigation and measurement, to the determination of specific heats of gases and the degree of dissociation of combustion products at the high temperatures at which the working fluid of the engine is employed. (Reference 9, p. 536, Reference 10, p. 513, Reference 11, p. 641.)

The deviations from a kinetic expression, $s=k_F$ $[F]^{n_1}$ $[O_2]^{n_2}$, here noticeable and measurable in the results given above, may prove of similar value concerning a more efficient combustion of hydrocarbon fuels in
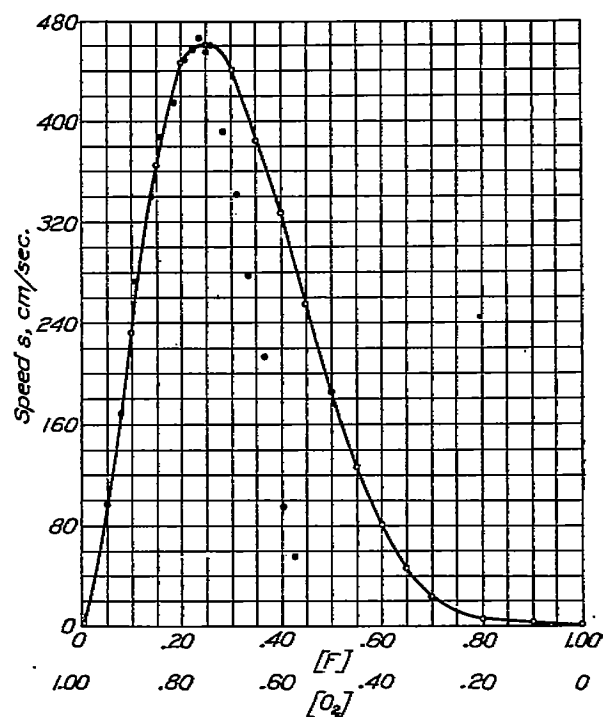

FIGURE 11.—Is a graph plotted from the values given in Table XI. In this case the fuel was made up of three active components, carbon monoxide, methane, and butane taken in equal proportions by volume. The continuous curve in the figure corresponds to the equation $s=23532$ $[F]^{1.71}$ $[O_2]^{5.28}$. Observed values are represented by dots, •

the gas engine. (Reference 8, p. 16.) The problem here is of the same order as the problem of the determination of an equilibrium in an autoclave used in the industrial synthesis of fuels: Given the pressure and temperature within the container, the composition of the hydrocarbon and the other gases of the mixture,

to determine the resulting products (equilibrium) at the temperature and pressure of the autoclave.

Explosive limits.—Quite incidental to the line of study that is the subject of this report, the results here given, together with many other results obtained with other gases and with other fuel combinations in the study of the kinetics of the gaseous explosive reaction at constant pressure, cover the range of "explosive limits" of those gases for the conditions of constant pressure imposed on the reaction. The subject is referred to here because investigations having in view the determination of explosive limits and seeking for the results obtained a fundamental relationship between fuel composition and range of inflammability have employed constant volume methods that involve great changes in pressure during the transformation and produce in the active gases the flame is entering not only indeterminate changes in their concentrations but also violent and erratic movement of the gases carrying the flame. There is no way under these (constant volume) conditions to distinguish between the flame movement due to the mass movement of the gases it is transforming and the essential part of its motion—namely, its motion relative to the gases themselves.

The marked disagreement noticeable in the results of different investigations carried out under conditions of constant volume called forth the following observation concerning the experimental procedure by constant volume methods that has usually been followed: "The spread of the ordinary flame through the explosive gaseous mixture depends in every respect upon the influence of experimental conditions imposed on the reaction. It is, therefore, little to the point to speak of explosive limits or of flame velocity in terms of per cent composition of the explosive gases; every set of numerical results so obtained depends in large measure upon the mode of ignition and its position, upon the form and material of the inclosing container and upon the way by which the reaction runs its course—in short, upon the conditions imposed upon the reaction by the experimental device and method used. Under the same set of constant physical conditions, the same set of numerical results may well be obtained. The explosive limits of a number of gaseous mixtures have been repeatedly investigated, often under very different conditions and in consequence yielding very different results." (Reference 12, p. 637.)

The above observation may well apply to all kinetic studies of gaseous explosive reactions made under constant-volume conditions. Under these conditions indeterminate pressure changes set up in the active gases by the explosion and by reflected impulse waves render the concentrations of the active gases the flame may be entering at any instant indeterminate also.

So far as the writer is aware, no investigations with a view of finding a relation, if such exist, between explosive range and fuel composition have been carried out by constant-pressure methods. Without going into detail it may be seen that the results given in this report all cover the explosive range of the fuels studied. These experimental results, as well as the theoretical figures accompanying them, all clearly point to a fundamental relation connecting the magnitude of explosive range with the value of the partial pressure of the fuel for maximum energy $[F]_{max}$. Stated in general terms the relation is: The greater the value of $[F]_{max}$, the greater is the explosive range. The curves for the heavier hydrocarbons are all narrow, since their complete combustion requires so much oxygen. The actual experimental curves are still narrower, owing to the effect of the secondary reaction on the rich side. The curve for the CO, O_2 reaction is broad, since little oxygen is required for complete combustion. These statements may be expressed numerically:

$$[F]_{CO, max.} = 0.667, \text{ its explosive range is } 0.93 - 0.20 = 0.73$$
$$[F]_{CH4 max.} = 0.333, \text{ its explosive range is } 0.47 - 0.14 = 0.33$$
$$[F]_{C4H10 max.} = 0.133, \text{ its explosive range is } 0.24 - 0.04 = 0.20$$

Fuels of intermediate $[F]_{max}$— values show intermediate explosive ranges.

BUREAU OF STANDARDS,
WASHINGTON, D. C.,
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